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(54) Electrically conductive polymeric materials and uses thereof.

(57) Structures containing conducting polymers and methods of fabrication thereof. Electrical conductivity can be induced in polymers selected from the group consisting of substituted and unsubstituted polyanilines, poly-paraphenylenevinylenes, substituted and unsubstituted polythiophenes, substituted and unsubstituted poly-p-phenylene sulfides, substituted polyfuranes, substituted polypyrroles, substituted polyselenophenes, polyacetylenes formed from soluble precursors, combinations thereof and blends thereof with other polymers. The polymer contains a doping precursor, selected from the group consisting of onium salts, iodonium salts, triflate salts, borate salts, tosylate salts and sulfonyloxyimides. Conductivity can be selectively induced in the polymer by selectively doping upon selective exposure to a source of energy such as electromagnetic radiation, an electron beam and heat. The electrically conductive polymers of the present invention are useful as electron discharge layers for electron beam applications, such as SEM observations, as electromagnetic interference coatings on dielectric surfaces and as an electron beam resist which acts as a discharge layer.

FIG. 10



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ELECTRICALLY CONDUCTIVE POLYMERIC MATERIALS AND USES THEREOF

This invention relates to electrically conductive polymers, electrically conductive resists, uses thereof and structures fabricated therewith. More particularly, this invention relates to electrically conductive substituted and unsubstituted polyanilines, substituted polyparaphenylenevinylenes, substituted and unsubstituted polythiophenes, polyazines, substituted polyfuranes, substituted polypyrroles, substituted poly-
 5 selenophene, substituted and unsubstituted poly-p-phenylene sulfides and polyacetylenes formed from soluble precursors and to selectively forming conducting patterns in these materials and the use of these materials as an electrical discharge layer.

Electrically conducting organic polymers have been of scientific and technological interest since the late 1970's. These relatively new materials exhibit the electronic and magnetic properties characteristic of
 10 metals while retaining the physical and mechanical properties associated with conventional organic polymers. Technological applications of these polymers are beginning to emerge.

The article entitled "Photoinitiated Doping of Polyacetylene", T. Clarke et al., J.C.P. Chem Comm., 1981, p.384, describes insoluble polyacetylene selectively doped with proton acids. The polyacetylene is
 15 impregnated with one of the group of triarylsulfonium and diaryliodonium which are inert to the polyacetylene but which on irradiation with UV light undergo a photochemical reaction leading to the doping of the polyacetylene to make it conductive. The impregnated film can be selectively exposed to light through a mask to selectively dope selected regions of the polymer. Polyacetylene is not suitable as a
 20 resist material since the polyacetylene is not soluble. For a polymer to be suitable as a resist material it must be capable of having a preselected pattern formed therein, for example on exposure to radiation, with either the exposed or unexposed region being soluble in a solvent while the other of the exposed or unexposed region is insoluble in the solvent.

The article entitled "Photochemically Doped Polypyrrole" of S. Pitchumani et al., J. Chem. Soc., Chem. Commun., 1983, p. 809, describes photochemically doped polypyrrole using diphenyliodoniumhexafluoroar-
 25 senate as photochemical dopant. Doping was accomplished by immersion of the polypyrrole substrate in a solution containing the photochemical dopant in methylene dichloride followed by irradiation with a mercury arc. Polypyrrole is also not suitable for a photoresist material since it is insoluble.

In both the article of Clarke et al. and the article of Pitchumani et al. an insoluble solid polymer is immersed in a solution containing a dopant material. The dopant material and the solvent are absorbed into
 30 the surface of the material. In both cases the solvent in combination with the dopant is exposed to light to render the irradiated part of the polymer electrically conducting. Because of the non-soluble nature of the polymers, the dopants can only be impregnated or absorbed into the surface of the polymer film.

The article entitled "Polyaniline; Processability From Aqueous Solutions and Effective Water Vapor on Conductivity" to M. Angelopoulos et al., Synthetic Metals, 21 (1987) pp.21-30, and the article entitled
 35 "Polyaniline: Solutions, Films, and Oxidation State" to M. Angelopoulos et al., Mol. Cryst. Liq. Cryst. 160-151 (1988), describe a chemically synthesized emeraldine base form of polyaniline which is soluble in various solvents. The emeraldine base is doped by reacting the emeraldine powder or film with aqueous acid solution for several hours, for example, aqueous acetic acid or aqueous HCl.

One problem associated with electron beam lithography is charging of the electron beam resist. This is particularly significant in microelectronic applications. In microelectronic applications, a pattern in a
 40 dielectric layer or an electrically conducting layer can be formed by depositing a resist material thereover. A commonly used method of selectively removing the resist material is to selectively expose the resist material to an electron beam. The resist material in the exposed region is either made soluble or insoluble upon exposure to the electron beam radiation. The solubility of the unexposed region is opposite that of the exposed region. Therefore, the exposed or the unexposed region can be removed. The resist material is
 45 typically a dielectric. When an electron beam is directed at a dielectric surface, charges from the electron beam accumulate on the surface creating an electric field which distorts the electron beam on the surface resulting in a loss of precision and displacement errors. To avoid charging the resist, it is common practice in the art to coat the resist, prior to electron beam exposure, with a thin conducting metal layer. Most metals, e.g. Au and Pd, are difficult to remove. In some cases the metal deposition process can degrade
 50 the lithographic properties of the resist due to heat and stray radiation during deposition.

The conductive polymer materials of the present invention can also be used as an electrical discharge layer for scanning electron microscopic applications. Typically, when a sample is being analyzed under a scanning electron microscope a thin metal layer is coated onto the sample. A commonly used metal layer is gold or a mixture of gold with other metals. This thin metallic layer acts as an electrical discharge layer to prevent the accumulation of electrical charge on the surface of the sample being examined. When a

metallic material is used as an electrical discharge layer it cannot be easily removed, therefore, the sample being examined must be discarded. This is particularly costly in microelectronic applications where it may be desirable to examine a semiconductor chip or semiconductor chip packaging substrate with an electron microscope where the chip or substrate is functional and useful. Depositing a thin metallic layer onto a substrate would render the chip or substrate not usable.

It is therefore an object of this invention to provide an electron beam resist material which functions as an electrical discharge layer.

It is another object of this invention to provide a method of forming a solid solution of a polymer which is selectively transformed to the conducting state by being selectively exposed to a source of energy.

It is yet another object of this invention to provide a resist material whose solubility and conductivity are dependent upon a dopant species generated by exposure of a dopant precursor to energy.

It is still another object of this invention to provide a conductive polymeric electromagnetic interference layer.

It is a further object of this invention to provide an electrical discharge layer for substrates exposed to electron beam radiation, wherein the discharge layer is removable.

These and other objects of the present invention are achieved by the structure disclosed in claim 1, the methods disclosed in claim 7 and 17 and the resist disclosed in claim 19.

Selected regions of films of the materials of the present invention can be made conducting upon the selective exposure to a source of energy. These materials can be used to make a patternable conductive resist material and can be used as an electrostatic discharge layer, or as an electromagnetic interference (EMI) layer on the surface of a substrate. Because of the electrostatic properties of these materials they can be used as an electron beam resist which acts as its own discharge layer. Moreover, since the materials of the present invention can be readily removed from a surface on which they are deposited, they can be used as a removable electrostatic discharge layer disposed on a dielectric surface under electron beam microscopic examination, for example in a scanning electron microscope (SEM). A removable electrostatic discharge layer permits SEM analysis without destroying the sample.

According to the present invention where conductive polymeric materials are used as a resist material the dopant reagent and polymer are mixed in a solvent which is thereafter dried to remove the solvents to form a solid solution of the dopant reagent and the polymer. The solid solution is then selectively exposed to energy, for example, electromagnetic radiation, heat or an electron beam, which causes the reagent to decompose to dope those regions of the polymer which are exposed to the energy forming a conductive polymer in exposed regions. In the exposed region the polymer is rendered insoluble and in the unexposed regions the polymer is soluble and can thereby be removed to act as a negative photoresist which is selectively electrically conducting. A resist material of this kind is particularly useful for electron beam lithographic applications since the resist material can be its own discharge layer.

According to one aspect of the present invention, a resist material is provided which is on selective exposure to energy, for example electromagnetic radiation, an electron beam or heat, rendered insoluble and at the same time electrically conducting. The exposed regions are insoluble and conducting and the unexposed regions are soluble and nonconducting. When the source of energy generating the pattern is an electron beam, the pattern which is conducting forms an electron discharge path preventing distortion of the writing beam. If the dielectric layer on which the resist is deposited is thin, the discharge path does not have to be grounded. This avoids the requirement of depositing a metal layer to act as a discharge layer.

The polymer materials which are made electrically conductive according to the present invention have additional utility in providing an easily processable and low cost EMI (electromagnetic interference) layer which can provide shielding of electrical components from electrical noise.

A broad aspect of this invention is a polymeric material which has selected regions which are electrically conductive and insoluble and wherein non-electrically conductive regions are soluble.

In a more particular aspect of the present invention, the polymeric material has a partially conjugated π system which is extended by the addition of dopants to the polymeric material to provide at least enough π conjugation so that the π conjugated parts of a molecule of the polymer are substantially in contact with the π conjugated parts of an adjacent molecule.

In another more particular aspect of the present invention, the polymer is selected from substituted polyparaphenylenes, substituted or unsubstituted polyanilines, substituted polythiophenes, polyazines, substituted or unsubstituted poly-p-phenylene sulfides, substituted polypyrroles, substituted polyselenophene, polyacetylenes formed from soluble precursors, combinations thereof and blends thereof with other polymers.

In another more particular aspect of the present invention, a reagent containing a doping species is contained within the polymer matrix. The doping species is capable of dissociating upon the application of

energy, such as electromagnetic radiation, an electron beam and heat. The dissociated species dopes the polymer making it electrically conductive.

In another more particular aspect of the present invention, the dopant species is selected from the group of onium salts, iodonium salts, borate salts, tosylate salts, triflate salts and sulfonyloxyimides.

5 Another more particular aspect of the present invention is a method of writing and developing a negative image in a polymer wherein the undeveloped portions of the polymer are electrically conducting.

In another more particular aspect of a method according to the present invention, a solution is formed from a polymer having an extended π conjugated system with a doping species and a solvent. The solution is deposited onto the surface of a substrate, dried to remove the solvent leaving a solid solution of the polymer and the doping species on the surface. The solid solution is selectively exposed to energy, for
10 for example, electromagnetic radiation, electron beam radiation or heat, to render the selectively exposed regions electrically conductive. The unexposed regions are thereafter removed in a solvent leaving a pattern of an electrically conductive polymer.

In another more particular aspect of the present invention, a substrate is coated with the electrically
15 conductive polymers according to the present invention, wherein the electrically conductive polymer coating acts as an electrical discharge layer.

So by the electrically conducting polymeric materials according to the present invention, a functional sample can be coated with the polymer, subjected to examination under an electron microscope and thereafter the electrically conductive polymer can be easily removed permitting electron microscopic
20 examination of the functioning part and permitting it to be subsequently used.

In another more particular aspect of the present invention, the polymers with the dopant therein according to the present invention are disposed on the surface of a sample for electron beam microscopic examination to function as an electrical discharge layer eliminating distortion from accumulated charge on the electron beam irradiated surface.

25 The above and other objects, features and advantages will become more apparent from the following detailed description of the preferred embodiments and the figures appended thereto, wherein

Fig. 1 is a UV-visible spectra of the emeraldine base form of polyaniline,

Fig. 2 is the UV-visible spectrum of the emeraldine base form of polyaniline containing an onium salt,

Fig. 3 is the UV-visible spectrum of composition of Fig. 2 after exposure to light at about 240 nm,

30 Fig. 4 shows UV light induced conducting lines in an emeraldine base/onium salt polymer of the present invention,

Fig. 5 shows the pattern shown in Fig. 4 developed,

Fig. 6 shows a low resolution SEM of a dielectric mask,

Fig. 7 shows a low resolution SEM of the mask of Fig. 6 after the mask has been coated with a
35 conductive polyaniline material,

Fig. 8 is a high resolution SEM dielectric mask,

Fig. 9 is a high resolution SEM of the mask of Fig. 8 coated with an electrically conducting polyaniline material, and

40 Fig. 10 is a photograph of a polyaniline polymer containing an onium salt after exposure to an electron beam to form conducting lines therein shown as the dark pattern.

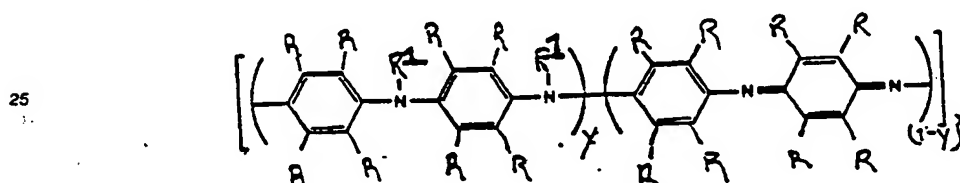
One embodiment of the present invention is a polymeric material which can be used as a negative resist material. The polymer is disposed onto a substrate and selectively exposed to a source of energy. The energy renders the exposed regions insoluble as compared to the unexposed regions and the exposed regions are rendered electrically conductive. These materials are useful as negative resists for microelectronic applications, such as patterning a dielectric or metal layer on the surface of a semiconductor chip or semiconductor chip package substrate. The use of these materials as resist material has particular utility in
45 electron beam lithography.

Resist materials are generally polymers which are dielectrics. If an electron beam is used to write a pattern in a dielectric resist material, electrons can accumulate on the surface of the dielectric resist. These
50 electrons create an electric field which results in distortion of the electron beam which is writing the pattern. State of the art electron beam lithography uses electron beams having a cross-sectional size in the order of a micron and less. It does not take much locally accumulated charge to create a distortion in such a small cross-sectional beam. To avoid this problem it is common practice in the art to deposit over a resist material a thin layer of metal. We have discovered a way of avoiding depositing a thin layer of metal onto a
55 resist material to avoid the charging problem. The polymers of the present invention can be used as a direct substitute for the metal layer. The polymer is deposited onto the surface of the electron beam resist and exposed to a source of energy to render it conducting. The conducting polymers act as a discharge layer.

The polymers used to fabricate the resist materials of the present invention contain a partially conjugated π system. A solution is formed of the polymer. To the solution is added a doping species (dopant precursor) which on exposure to energy generates a dopant which dopes the polymer to the conducting state. The addition of the dopant results in an expansion of the extent of the conjugated π system in the individual polymer molecule. It is not necessary to extend the conjugated π system over the full extent of the molecule. It is only necessary to sufficiently extend the π conjugated system of an individual molecule so that after the solvent is removed the π conjugated part of an individual molecule is adjacent to a part of the π conjugated part of an adjacent molecule. In the π conjugated system an electron is essentially delocalized over the entire π conjugated bonds. These electrons are more loosely bound and are available for electrical conduction. When an electric field is applied, an electron can flow along an individual molecule and hop from one molecule to an adjacent molecule in a region where the π conjugated parts of the adjacent molecules overlap.

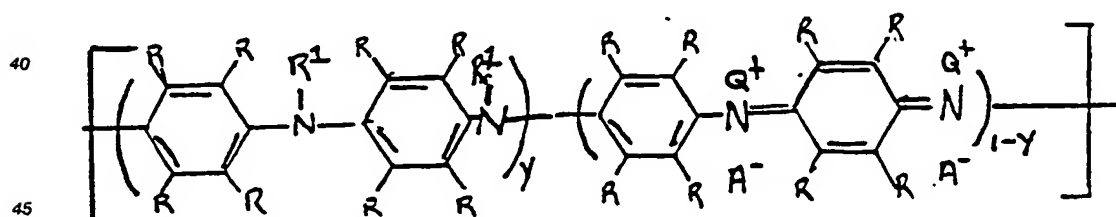
To form a negative resist according to the present invention a π conjugated system must be soluble when not exposed to the dopant and insoluble when exposed to the dopant. One possible explanation for the change in solubility upon exposure to the dopant is the following. Dopants can be a cationic species. The dopant transfers positive charges to the π conjugated parts of the polymer through protonation, pseudo protonation or oxidation. The polymer now has positive charges on the backbone and then combines with anions to form ion pairs. It is more difficult for a solvent to have enough solvation energy for these ion pairs than for the pristine polymer.

One type of nonconducting polymer useful to practice the present invention is a substituted or unsubstituted polyaniline having the following general formula:

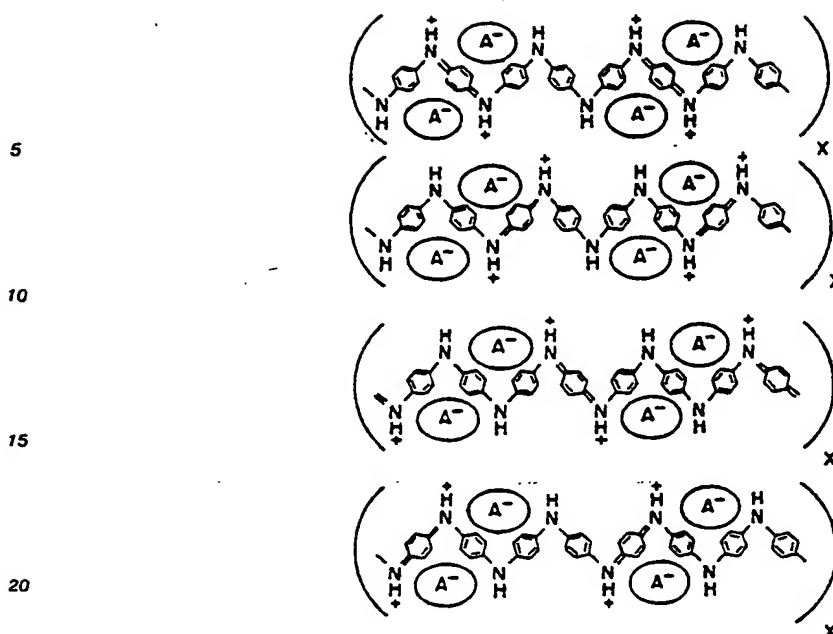


wherein each R can be H or any organic or inorganic radical; each R can be the same or different; $x \geq 1$; preferably $x \geq 2$ and y has a value from 0 to 1. Examples of organic radicals are alkyl or aryl radicals. Examples of inorganic radicals are Si and Ge. This list is exemplary only and not limiting. The most preferred embodiment is the emeraldine base form of the polyaniline wherein y has a value of 0.5.

If the polyaniline base is exposed to a cationic species QA, for example a protic acid wherein Q is hydrogen, the nitrogen atoms of the imine part of the polymer become substituted with the Q cation to form an emeraldine salt as shown in the following equation:



When a protic acid HA is used to dope the polyaniline, the nitrogen atoms of the imine part of the polyaniline are protonated. The emeraldine base form is greatly stabilized by resonance effects as is shown in the following sequence of equations:



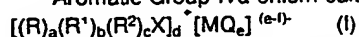
25 The charges distribute through the nitrogen atoms and aromatic rings making the imine and amine nitrogens indistinguishable. For the sake of simplicity the above sequence of equations was shown with a protonic acid HA. However, a cationic species represented by QA can also be used whereas Q is a cation selected from organic and inorganic cations, for example, an alkyl group or a metal, being most preferably H.

30 The emeraldine base form of polyaniline is soluble in various organic solvents and in various aqueous acid solutions. Examples of organic solvents are dimethylsulfoxide (DMSO), dimethylformamide (DMF) and N-methylpyrrolidinone (NMP). This list is exemplary only and not limiting. Examples of aqueous acid solutions are 80% acetic acid and 60-88% formic acid. This list is exemplary only and not limiting. Substituted polyanilines are soluble in more solvents such as chloroform and methylenechloride.

35 A powder of the emeraldine base is mixed in a solvent with a radiation sensitive onium salt. Upon exposure to radiation the onium salt produces free acid which protonates the emeraldine base to yield an emeraldine salt. Anything that generates a cationic species upon electromagnetic or electron beam radiation can dope the polyaniline polymer.

40 Examples of suitable onium salts include aromatic onium salts of Group IVa elements discussed in U.S. Patent 4,175,972, disclosure of which is incorporated herein by reference, and aromatic onium salts of Group Va elements discussed in U.S. Patent 4,069,055, disclosure of which is incorporated herein by reference.

Aromatic Group IVa onium salts include those represented by the formula:

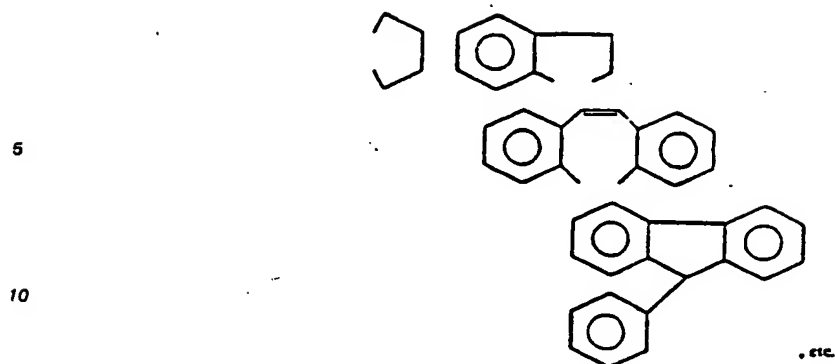


45 where R is a monovalent aromatic organic radical, R' is a monovalent organic aliphatic radical selected from alkyl, cycloalkyl and substituted alkyl, R² is a polyvalent organic radical forming a heterocyclic or fused ring structure selected from aliphatic radicals and aromatic radicals, X is a Group IVa element selected from sulfur, selenium, and tellurium, M is a metal or metalloid, Q is a halogen radical, a is a whole number equal to 0 to 3 inclusive, b is a whole number equal to 0 to 2 inclusive, c is a whole number equal to 0 or 1, where the sum of a + b + c is a value equal to 3 or the valence of X,

50 d = e - f

f = valence of M and is an integer equal to from 2 to 7 inclusive, e is > f and is an integer having a value up to 8.

55 Radicals included by R are, for example, C₆₋₁₃ aromatic hydrocarbon radicals such as phenyl, tolyl, naphthyl, anthryl, and such radicals substituted with up to 1 to 4 monovalent radicals such as C₁₋₃ alkyl such as methyl and thyl, substituted alkyl such as -C₂H₄OCH₃, -CH₂COOC₂H₅, -CH₂COCH₃, etc. R² radicals include such structures as:



15 Complex anions included by $\text{MQe}^{(e-)}_{\text{I}}$ of Formula I are, for example, BF_4^- , PF_6^- , SbF_6^- , FeCl_4^- , SbCl_6^- , BiCl_5^- , AlF_6^{3-} , GaCl_4^- , InF_4^- , TiF_6^- , ZrF_6^- , etc., where M is a transition metal such as Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, Sc, V, Cr, Mn, Cs, rare earth elements such as the lanthanides, for example, Ce, Pr, Nd, etc., actinides, such as Th, Pa, U, Np, etc. and metalloids such as B, P and As.

20 Group IVa onium salts included by Formula I are, for example:

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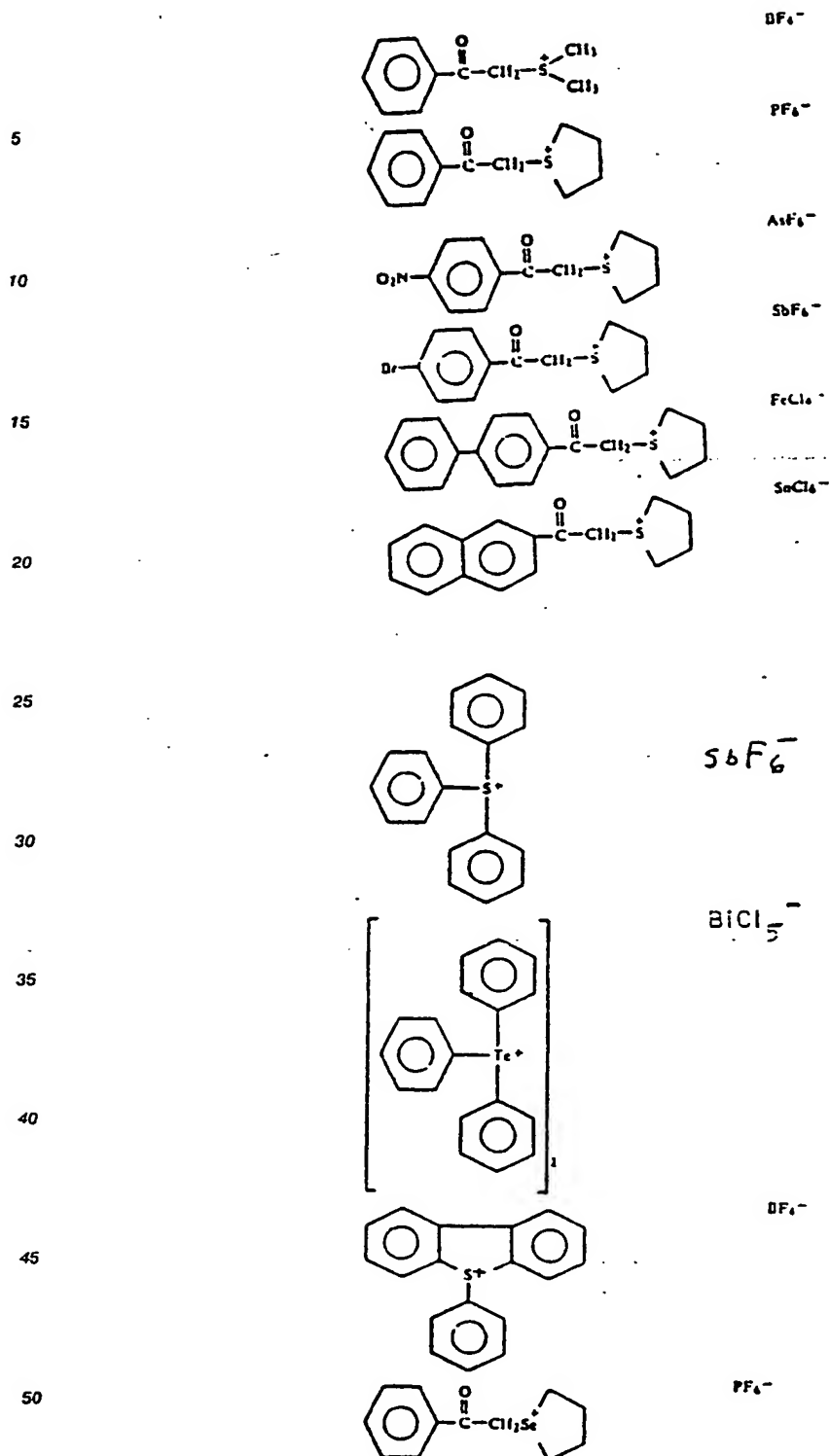
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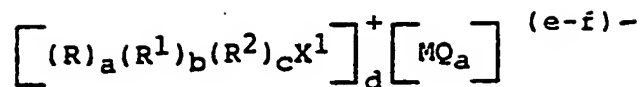
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Aromatic group Va onium salts include those represented by the formula:

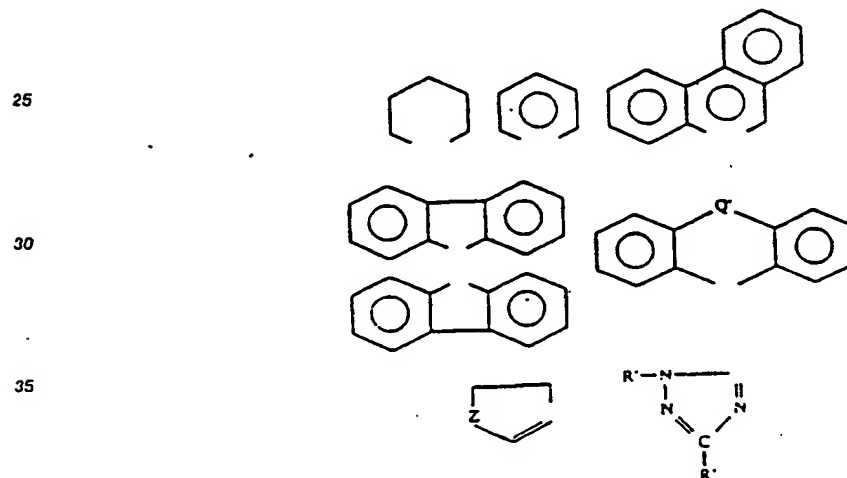


5 where R is a monovalent aromatic organic radical selected from carbocyclic radicals and heterocyclic radicals, R¹ is a monovalent organic aliphatic radical selected from alkyl, alkoxy, cycloalkyl and substituted derivatives thereof, R² is a polyvalent organic radical forming an aromatic heterocyclic or fused ring structure with X¹, X¹ is a Group Va element selected from N, P, As, Sb, and Bi; M is a metal or metalloid, Q is a halogen radical, a is a whole number equal to 0 to 2 inclusive, c is a whole number equal to 0 to 2 inclusive, and the sum of a+b+c is a value equal to 4 or the valence of X¹,

d = e-f

f = valence of M is an integer equal to from 2 to 7 inclusive, e is >f and is an integer having a value up to 8. Radicals included by R are, for example, C₍₆₋₁₃₎ aromatic hydrocarbon radicals such as phenyl, tolyl, naphthyl, anthryl and such radicals substituted with up to 1 to 4 monovalent radicals such as C₍₁₋₈₎ alkoxy, C₍₁₋₈₎ alkyl, nitro, chloro, and hydroxy; arylacyl radicals such as phenylacyl; arylalkyl radicals such as pyridyl and furfuryl; R¹ radicals include C₍₁₋₈₎ alkyl, C₍₃₋₈₎ cycloalkyl, substituted alkyl such as haloalkyl, for example, choroethyl; alkoxy such as -OCH₂C₆H₅ and -OCH₃; alkoxyalkyl such as -CH₂COCH₃; alkylacyl such as -CH₂COOC₂H₅; ketoalkyl such as -CH₂COCH₃.

Radicals included by R² are, for example:



40 where Q is selected from O, CH₂, N, R, and S; Z is selected from -O-, -S- and



and R' is a monovalent radical selected from hydrogen and hydrocarbon. Complex anions included by MQ_e^{(e-f)-} are, for example, BF₄⁻, PF₆⁻, AsF₆⁻, FeCl₄⁻, SnCl₆²⁻, SbCl₆²⁻, BiCl₅⁻, where M is more particularly a transition metal such as Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, Sc, V, Cr, Mn and Co; rare earth elements such as the lanthanides, for example, Ce, Pr and Nd; actinides such as Th, Pa, U and Np; and metalloids such as B, P and As.

Anions which are slightly hydrolyzed, e.g. SbF₅OH⁻ are considered to be the full equivalent to the inhydrolyzed form of the anion for the purposes of the present invention.

Example 1

To 30 ml of NMP (N-methyl pyrrolidinone) was added 1.5 g of an emeraldine base powder and 9 g of triphenylsulfonium hexafluoroantimonate. The solution was spin-coated onto quartz and silicon wafers to yield a film of approximately 240 nm (2400 angstroms). Fig. 1 shows a uv/visible spectrum of this film. The peaks at 320 nm and 610 nm are characteristic of emeraldine base as seen by comparison with the uv/visible spectrum of emeraldine base alone shown in Fig. 2.

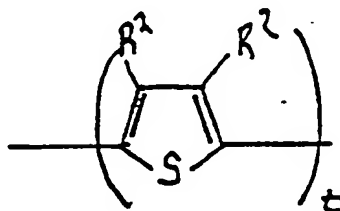
The film is dried to remove the solvent. Upon exposure to radiation using a 240 nm filter which was selected for the sensitivity of the onium salt used, the uv/visible spectrum of the emeraldine base film contained the onium salt changes. (It is not necessary to filter the radiation, flooding exposure at all wavelengths can be used.) The peaks characteristic of the insulating emeraldine base decrease and there is an appearance of an absorption peak around 850 nm which is characteristic of the conducting emeraldine salt. The conductivity of the exposed film was measured using a four point probe to be approximately $1.6 \text{ ohm}^{-1}\text{cm}^{-1}$. It will be recognized by those of skill in the art that the conductivity can be controlled by controlling the amount of onium salt added to the polyaniline and by the amount of time to which the polymer and onium salt combination is exposed to the radiation. The polyaniline becomes insoluble upon exposure. In prior art methods, an emeraldine base is mixed in solution with an acid which protonates the emeraldine base in solution. In contradistinction, according to the present invention, an onium salt is mixed with the emeraldine base solution, the onium salt does not protonate the polymer to be conductive at this point. The solution is disposed onto the surface of a substrate and the solvent is removed by heating to result in a solid solution of the polymer with the onium salt embedded therein. The polymer at this point is still not conductive. Only after exposure to electromagnetic radiation, most preferably UV light, or an electron beam does the polymer become conducting.

Fig. 4 shows a photograph showing an example of the polyaniline onium salt polymer mixture exposed to radiation through a mask to form conducting lines which appear dark in the figure. There is a color change upon exposure. The nonconducting form is blue and the conducting or exposed form is green. The width of these conducting lines are about 2 microns.

Fig. 5 is a photograph of the pattern of Fig. 4 with the parts of the polymer which have not been exposed to radiation removed by exposure to an organic solvent such as those listed above. Therefore, a negative resist material resulting in conducting lines has been formed.

Fig. 10 shows a photograph of a polyaniline onium salt combination which has been selectively exposed to an electron beam to form conducting line having conductivity of $10^{-2} \text{ OHM}^{-1}\text{CM}^{-1}$, width $0.5 \mu\text{m}$ and $1.0 \mu\text{m}$ spacing.

The present invention is applicable to a substituted polythiophene. Polythiophenes have the general formula:



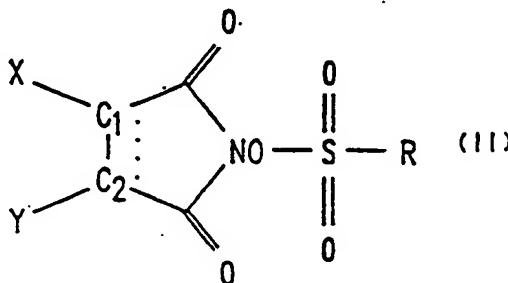
wherein each R^2 is H or any organic or inorganic radical; wherein $t \geq 1$ and wherein at least one R^2 is not H.

It is known in the art that conducting forms of polythiophene are soluble in organic solvents such as nitrobenzene, THF : CH_2Cl_2 : CH_3CCl_3 (4:1:1) and in tetrahydronaphthalene. Since these solvents have either a high boiling point or are poisonous, they are unacceptable for a manufacturing environment. It is also known in the art that the polythiophene can be converted to a conducting form upon treatment with a solution of I_2 , NOBF_4 , AsF_5 and SbF_5 . These chemicals can corrode electronic components and therefore are unsuitable for electronic applications. Also, the use of these chemicals requires an additional step in the process, first, the polythiophene must be deposited on a substrate and then treated with these chemicals. In contradiction, according to the present invention an onium salt, iodonium salt, a triflate salt, a borate salt, a tosylate salt, a sulfonyloxymide, or any reagent (referred to herein as a dopant precursor) or oxidizing (a dopant) which dissociates upon exposure to a source of energy to a cationic species is mixed in solution with the polythiophene, deposited on the substrate, dried to remove the solvents and then exposed to either electromagnetic radiation, for example UV radiation, an electron beam, or heat, to convert the polymer to the conductive state.

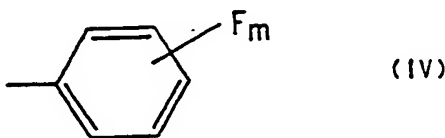
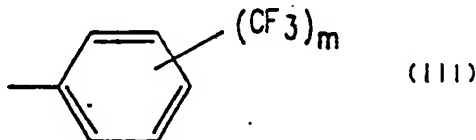
It is believed that the acid generated by the photodecomposition or electron beam decomposition of the

onium salt or the sulfonyloxyimide combines with oxygen to oxidize the polythiophene polymer. Polythiophene has a partial conjugated π system. It is believed that the oxidation caused by the decomposed onium salt or the sulfonyloxyimide extends the conjugated π system to induce conductivity in the polythiophene.

Sulfonyloxyimides useful to practice the present invention have the following general formula:



wherein R is selected from the group consisting of $-\text{CF}_3$, $-\text{CF}_2\text{CF}_3$, $-\text{CF}_2\text{CF}_2\text{H}$, $-(\text{CF}_2)_n$ where $n=1$ to 4, where Z is H, alkyl or aryl,



where m is from 1 to 5, and where X and Y (1) form a cyclic or polycyclic ring which may contain one or more hetero atoms, (2) form a fused aromatic ring, (3) may be independently H, alkyl or aryl, (4) may be attached to another sulfonyloxyimide containing residue, or (5) may be attached to a polymeric chain or backbone.

Example 2

About 345.6 mg of poly(3-butylthiophene) and 230 mg of triphenyl sulfonium hexafluorantimonate in 4 ml xylene and 2 ml NMP were mixed on a roller at 56°C for one hour. The solution was spin-coated on a silicon wafer containing 500 nm (5000 Å) silicon oxide with spin speed 1200 RPM for 10 seconds. The wafer containing this polymer coating was then baked in a convection oven for 30 minutes at 100°C . After baking it was then subjected to deep UV exposure for 30 minutes. The film turned to black color after exposure. The wafer was then further baked in an oven for 2 hours at 100°C . A conductivity of approximately 0.02 S/cm was measured with 4-probe on the film (1.5 μm).

Example 3

About 156 mg of 3-methylthiophene-3-butylthiophene-copolymer (PMBT) in 3 ml xylene was mixed on a roller at 56°C . The solution was filtered through a funnel having frit size 0.9 - 1.5 μm . 117 mg of

trifluoromethylsulfonylbicyclo (2,2,1)-hept-5-ene-2,3-dicarboximide (MDT) were added to the solution and mixed on roller for 45 minutes. The solution was spin-coated on SiO₂-Si wafer with spin rate 2000 RPM for 30 seconds. The wafer was then subjected to UV exposure for 10 minutes and the hot plate for 1 minute at 89 °C. A conductivity of 0.04 S/cm was measured on the polymer (approximately 0.4 μm) using 4-Probe.

5

Example 4

About 600 mg of PMBT was dissolved in a copious amount of xylene (200 ml) then filtered through pressure filter funnel (F frit). The solvent was evaporated and around 5 ml of PMBT in xylene solution was obtained. An amount of 76 mg MDT was added to the solution. The solution was filtered through a 1 μm filter tip using a gastight syringe. The polymer-MDT was spin-coated onto SiO₂-Si wafer and then subjected to UV exposure for 15 minutes. After the wafer was baked on a hot plate for 40 seconds at 90 °C, a conductivity of 0.1 S/cm was measured on the polymer using 4-probe.

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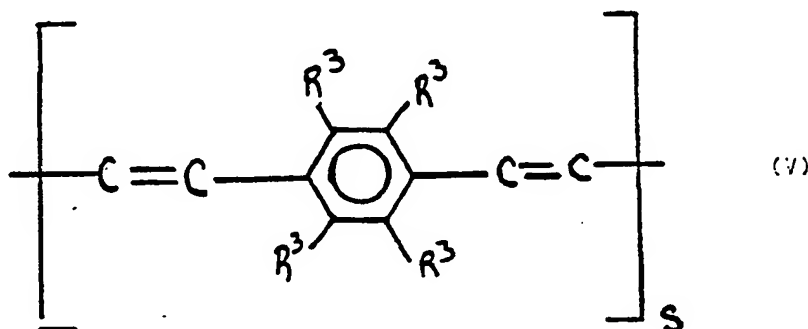
Examples 2, 3 and 4 can be repeated using an electron beam of about 200 μC/cm² to about 1 mC/cm² at about 25 KeV.

Polyparaphenylenevinylenes useful to practice the present invention have general formula (V) wherein each R³ is H or any organic or inorganic radical, and wherein s ≥ 1. Each R³ can be the same or different:

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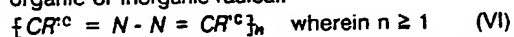
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Polyazines useful to practice the present invention have general formula (VI) wherein R² is H or an organic or inorganic radical.

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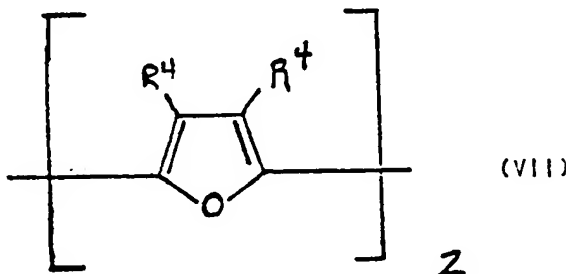


Polyfurans useful to practice the present invention have general formula (VII), wherein Z ≥ 1 and each R⁴ is H or any organic radical, and each R⁴ can be the same or different:

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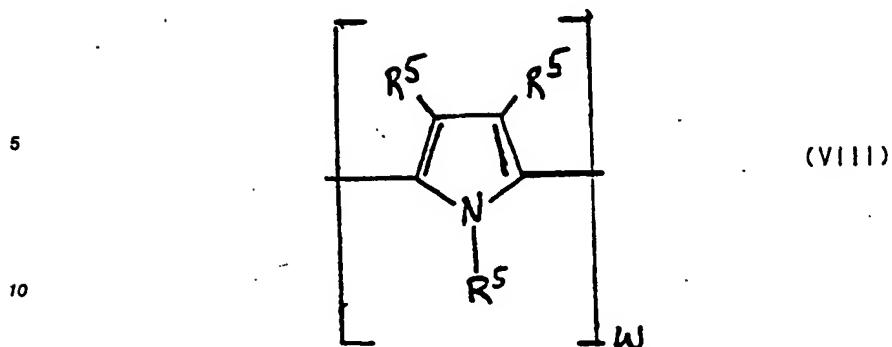
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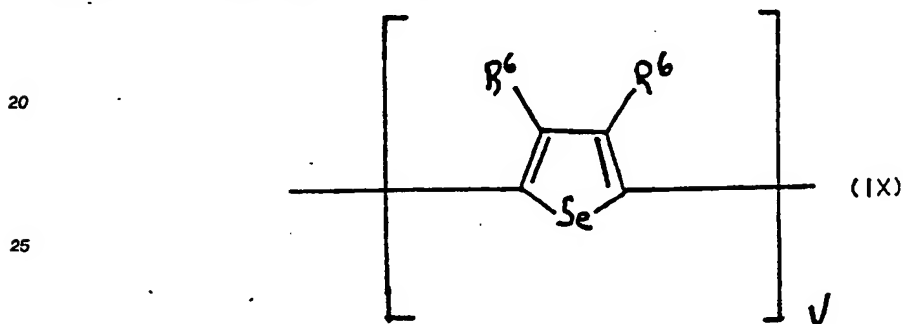


Polypyrroles which are useful to practice the present invention have general formula (VIII), wherein w ≥ 1, each R⁵ is H or any organic or inorganic radical; wherein each R⁵ can be the same or different:

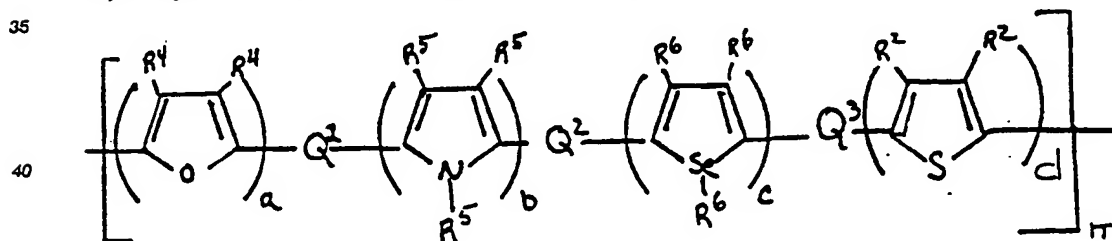
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15 Polyselenophenes useful to practice the present invention have general formula (IX), wherein $v \geq 1$, and each R^6 is H or any organic or inorganic radical and wherein each R^5 can be the same or different:



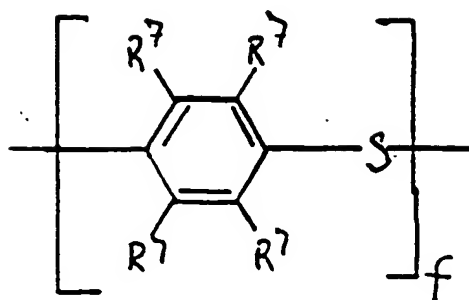
30 Examples of combinations of polythiophenes, polyfurans, polypyrroles and polyselenophenes useful to practice the present invention are represented by the following equations wherein R^4 , R^5 and R^6 are as defined above, wherein at least two of a, b, c and d are greater than or equal to 1; $m \geq 1$; Q^1 , Q^2 , Q^3 can be a vinylene group or a direct bond between adjacent constituents:



45 Poly-p-phenylene sulfides useful to practice the present invention are represented by the following general formula wherein each R^7 is H or any organic or inorganic radical and $f \geq 1$, each R^7 can be the same or different:

50

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The article entitled "New Routes to Processed Polyacetylenes", T. Swager et al. Polymer Preprints, Vol. 30, No. 1, p. 161, April 1989, the teaching of which is incorporated herein by reference describes methods of preparing polyacetylene from a soluble precursor. Polyacetylene is insoluble, therefore, as noted above a conductive resist cannot be made from polyacetylene directly. The soluble polyacetylene precursors of Swager et al. can be used in the structures and methods of the present invention to form a solid solution of polyacetylene and a reagent in which conductivity is induced after exposure to energy. Polyacetylene can be prepared from a number of precursors by the use of ring opening metathesis polymerization (ROMP). Cyclooctatetraene, a high boiling liquid, can be bulk polymerized to polyacetylene. In effect, this provides polyacetylene that can be processed as a viscous liquid. Substituted cyclooctatetraenes can be polymerized or co-polymerized to a soluble polymer that can be easily fabricated. Treatment of the polybenzvalene with Lewis acids results in the rearrangement to polyacetylene.

The polymers of the present invention can be easily spin coated onto a sample and exposed to energy to induce conductivity. The conductive polymers of the present invention can be used as top surface electrical discharge layers or as buried electrical discharge layers for electron beam applications. The conductive polymers according to the present invention are readily etchable in an oxygen plasma. When the polymers of the present invention are used as a buried discharge layer, a first resist layer is deposited onto a substrate, a polymer layer, according to the present invention, is deposited thereover and a second resist layer is deposited onto the polymer layer. The polymer layer can be made conducting by exposure to electromagnetic radiation, an electron beam or heat.

When the conducting polymers according to the present invention are used as a buried discharge layer underneath a dielectric resist layer, the top resist layer still charges up. When exposed to an electron beam the degree of charging depends upon the thickness of this top layer. If the resist material is not too thick, charge which accumulates in this top surface layer will leak to the conductive interlayer and flow to ground if the conductive interlayer is grounded. It has been found that the conductive interlayer does not have to be grounded to avoid a distortion of an incident electron beam. It is only necessary that the charge leaks away quick enough so as not to build up any significant potential at the electron beam target point.

It has been estimated that a surface conductivity of approximately $10^{-6} \text{ OHM}^{-1} \text{ cm}^{-1}$ is sufficient to avoid distortion of an incident electron beam of approximately 25 KeV with a dose of $15 \mu\text{C}/\text{cm}^2$. It has been found that this surface resistance will maintain the voltage difference between the target point on the top surface resist and a grounded buried conductive layer at a few volts, preferably less than 1.6V, when an electron beam voltage of approximately 20 KeV is used. For a 1 micron thick film a volume conductivity of about $10^{-2} \text{ OHM}^{-1} \text{ cm}^{-1}$ is needed to achieve a surface conductivity of this value. For a 0.1 nm (1,000 angstrom) thick film a volume conductivity of about $10^{-7} \text{ OHM}^{-1} \text{ cm}^{-1}$ is needed. We have found no distortion of an electron beam using 0.4 microns of a conductive discharge layer of a polythiophene having a surface conductivity of approximately $4 \cdot 10^{-6} \text{ OHM}^{-1}$ under 1 micron of resist even without the discharge layer being grounded. If the resist is grounded we expect a much lower conductivity is required.

The polythiophenes of the present invention have been found to be soluble in toluene and xylene and a little less soluble in polar solvents as for example THF (tetrahydrofuran), NMP and anisole. Very good mixing has been achieved between the polythiophenes and MDT in xylenes. Enhanced mixing in other solvents may be achievable by incorporating C-O-C linkages or other polar groups as side chains on the thiophene ring of the polymer.

Conductivity of the order of $10 \text{ OHM}^{-1} \text{ cm}^{-1}$ can be thermally induced in polymers according to the present invention. The polymeric conductivity is induced thermally by the use of reagents which on heating generate dopants, for example cations. The generated dopants dope the polymer to the metallic regime.

When amin triflate salts are heated they unblock to liberate a free acid, triflic acid, and the volatile

amine constituent, the temperature at which unblocking occurs depends on the volatility of the amine constituent. The general equation of an amine triflate salt is $\text{CF}_3\text{SO}_3\text{H} \cdot \text{NR}_3$. Upon the application of heat the salt unblocks to a free acid represented by chemical formula $\text{CF}_3\text{SO}_3\text{H}$ and the volatile amine represented by chemical formula R_3N . The triflic acid is then capable of protonating the polyaniline as described above.

5 Triflic acid is expected to protonate polyparaphenylenes, polyazines, polyfuranes, polypyrroles, polyselenophenes, poly-p-phenylene sulfides and polyacetylenes.

An NMP solution of the non-conducting polyaniline containing either diethyl ammonium trifluoromethane sulphonate or diisopropyl ammonium trifluoromethane sulfonate was spin-coated onto quartz wafers to yield thin films of approximately 0.2 nm (2,000 angstroms). The films were placed on a hot plate at a temperature range from about 80° to 90° C for 3 minutes by which time the films displayed a conductivity in the order of about 1 S/cm.

Other examples of triflate salts useful to practice the present invention which are thermally decomposable to a cationic species which can be used to generate dopants useful to practice the present invention includes the triflates, tosylates and borates of the following list:

- 15 $\text{CF}_3\text{SO}_3\text{H} \cdot \text{N}(\text{C}_6\text{H}_5)_3$
- $\text{CF}_3\text{SO}_3\text{H} \cdot \text{NH}_3$
- $\text{CF}_3\text{SO}_3\text{H} \cdot (\text{CH}_3)_3\text{N}$
- $\text{CF}_3\text{SO}_3\text{H} \cdot \text{C}_2\text{H}_5\text{NH}_2$
- $\text{CF}_3\text{SO}_3\text{H} \cdot (\text{C}_2\text{H}_5)_2\text{NH}$
- 20 $\text{CF}_3\text{SO}_3\text{H} \cdot (\text{C}_2\text{H}_5)_3\text{N}$
- $\text{CF}_3\text{SO}_3\text{H} \cdot (\text{i-C}_3\text{H}_7)_2\text{NH}$
- $\text{CF}_3\text{SO}_3\text{H} \cdot (\text{i-C}_3\text{H}_7)_2\text{N}(\text{C}_2\text{H}_5)$
- $\text{CF}_3\text{SO}_3\text{H} \cdot (\text{i-C}_3\text{H}_7)_2\text{N}(\text{C}_2\text{H}_5\text{OH})$
- $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{N}(\text{C}_2\text{H}_4\text{OH})$
- 25 $\text{CF}_3\text{SO}_3\text{H} \cdot \text{HN}[(\text{C}_4\text{H}_9)\text{O}]_2$
- $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{NC}(\text{CH}_3)_2\text{CH}_2\text{OH}$
- $\text{CF}_3\text{SO}_3\text{H} \cdot \text{HN}(\text{C}_2\text{H}_5\text{OH})_2$
- $\text{BF}_3 \cdot \text{C}_2\text{H}_5\text{NH}_2 (0.2\text{M})$
- $\text{CF}_3\text{SO}_3\text{CH}_3 \cdot \text{N}(\text{CH}_3)_3$
- 30 $\text{H}_3\text{C}(\text{C}_6\text{H}_4)\text{SO}_3\text{H} (0.1\text{M})$

This list is exemplary only and not limiting.

U.S. Patent application Serial No. 07/322,848 filed on March 14, 1989 to Brunscold et al. entitled "Chemically Amplified Photoresist", the teaching of which is incorporated herein by reference, describes other triflate compounds.

35 Since acid combines with oxygen to oxidize polymethylthiophene, thermal decomposition of triflate salts should dope polythiophene.

It will be recognized by those of skill in the art that the temperature applied and the time of duration of the applied temperature can be adjusted to achieve different values of conductivity. Any thermally decomposing species which generates a cation or oxide species can be used to thermally induce conductivity in the polymers of the present invention.

The electrically conducting polymers of the present invention have particular usefulness in electron microscopy. Electron microscopy is currently used in microelectronics to make observations and dimensional measurements on dielectric masks, for example, quartz/chromium masks used in optical lithography. Charging is caused by the incident electron beam. The current solution to avoid the charging problem is to deposit a thin layer of metal onto the mask. This is, however, a destructive method since complete removal of the metal layer is quite difficult if not impossible. Therefore, scanning electron microscopic observations and measurements are limited to scrapped pieces. Since the conducting polymers of the present invention are readily removable, for example by an oxygen plasma or by undoping in a base, for example, in 0.1M NH_4OH and dissolving off in a solvent, for example, NMP, they can be used as a discharge layer in SEM applications. Since the conductive polymers of the present invention are removable, they can be used as a discharge layer on the surface of masks, electronic devices such as semiconductor chips and semiconductor chip packaging substrates which are not scrap pieces.

Any of the conducting polymers according to the present invention can be used as a discharge layer to avoid distortion in electron beam microscopic observations. For example, a quartz/chromium mask was observed with a SEM at 10 KV at various resolutions. The same mask was coated with an NMP solution of polyaniline which was doped with 1N HCl to result in a conductivity of about 1 S/cm. The coated mask was heated to a temperature of about 80° C to drive off the solvent. The resulting film thickness was about 0.1 nm (1,000 angstroms). The polyaniline coated mask was observed with a SEM. Fig. 6 shows a 244 SEM of a

bare quartz/chromium mask. Fig. 7 shows a low resolution SEM of the same mask with a polyaniline coating. Fig. 8 shows a high resolution SEM of a bare mask. Fig. 9 shows a 16.4 KV SEM of the mask with a polyaniline coating. As can be readily seen from the Figs. 6-9, the masks which are coated with the conductive polyaniline have a substantially higher resolution than the uncoated mask.

Quite surprisingly it has been found that the minimum surface conductivity of the conductive polymer to avoid resolution distortion due to charging of the observed substrate is about 10^{-5} OHM^{-1} . Charging was not observed at 10 KV for a conducting polyaniline. Without the conductive coating charging is observed above 2 KV. It is quite surprising that materials having conductivities less than that of metals can act as a discharge layer when they are grounded or not grounded.

For image enhancement in a scanning electron microscope or the like conducting polymers can be made by techniques described herein. As described above a solution of a proton donor such as HCl and an emeraldine base form of a polyaniline can be mixed in solution which creates a conductive polymer. The solution can be disposed on the sample to be observed under an electron beam. The solvent can be driven off by the application of heat to form an electrically conductive polymer layer. Alternatively, the polymers fabricated according to the present invention can be used. The coated sample can either be exposed to heat or radiation to induce conductivity in the polymer or in the case of the electron beam sensitive cationic species, the electron beam used to make the SEM observation can induce the electrical conductivity in the polymer coating.

After SEM observation the polymer coating can be removed for example using a plasma etch, such as an oxygen plasma or in the case of a polyaniline doped with HCl the conductive polymer can be removed by a wash with for example a base, such as KOH, followed by an organic solvent, such as NMP.

The electrically conductive polymer materials of the present invention have additional uses such as an electromagnetic interference (EMI) coating on a dielectric surface. For example, electrical components are frequently contained within dielectric housings such as cabinets, molded plastics and the like. To reduce the susceptibility of the electronic components contained within the housing, the dielectric housing can be coated with the polymeric materials of the present invention. This EMI technique is easily implemented in a high volume manufacturing line and has very low cost. Continual EMI coatings contain expensive precious metals such as silver embedded in a polymer matrix.

In summary electrically conductive resist structures and materials have been described which act as their own electrostatic discharge layers. The electrical conductivity can be induced in the polymers of the present invention by exposure to sources of energy such as electromagnetic radiation, an electron beam and heat. The polymers according to the present invention contain π conjugated systems which are extended by exposing to dopants such as a cationic species. The preferred polymers are selected from the group of substituted and unsubstituted polyanilines, polyparaphenylenevinylenes, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors, combinations thereof and combinations thereof with other materials, blends thereof with other polymers and polymers thereof formed from soluble precursors. The polymers can be selectively doped. The polymers are useful as buried and surface electrical discharge layers for electron beam lithography applications and for discharge layers for electron microscopy applications, for example, scanning electron microscopy.

It is to be understood that the above described embodiments are simply illustrative of the principles of the invention. Various other modifications and changes may be derived by those of skill in the art which will embody the principles of the invention and fall within the spirit and scope thereof.

Claims

1. A structure comprising:

a polymeric material;

said polymeric material being selected from the group consisting of substituted and unsubstituted polyparaphenylenevinylenes, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors and combinations thereof and blends thereof with other polymers;

preselected regions of said polymer material being electrically conductive;

said conductive regions being substantially insoluble; and

the remainder of said material being substantially soluble.

2. The structure of claim 1, wherein said electrically conductive regions contain dissociated doping precursors selected from the group consisting of onium salts, iodonium salts, borate salts, tosylate salts,

triflate salts and sulfonyloxyimides, said dissociated precursors doping said polymeric material constituent.

3. The structure of claim 1, wherein said structure is a resist, selected from the group consisting of electron beam resist and optical resist.

4. The structure of claim 2 wherein said polymeric material is a polyaniline and wherein said precursor is selected from the group consisting of triphenylsulfonium hexafluoroantimonate, diethyl-ammonium trifluoromethane sulfonate and diisopropyl ammonium trifluoromethane sulfonate.

5. The structure of claim 4, wherein said polyaniline is an emeraldine base form of polyaniline.

6. The structure of claim 2 wherein said polythiophene is selected from the group consisting of poly(3-butylthiophene) and 3-methylthiophene-3-butylthiophene-copolymer and wherein said precursor is selected from the group consisting of trifluoromethylsulfonyloxybicyclo (2,2,1)-hept-5-ene-2,3-dicarboximide(MDT) and triphenyl sulfonium hexafluoroantimonate.

7. A method comprising:

forming a solid solution of a doping precursor selected from the group consisting of onium salts, triflate salts, iodonium salts, borate salts, tosylate salts and sulfonyloxyimides and a polymer selected from the group consisting of substituted or unsubstituted polyparaphenylenevinylenes, polyanilines, polyazines, polythiophenes, poly-p-phenyl sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors, combinations thereof and blends thereof with other polymers; and selectively exposing said solid solution to a source of energy selected from the group consisting of electromagnetic radiation, an electron beam and heat, inducing electrical conductivity within said selectively exposed regions.

8. The method of claim 7, wherein said polymer has a partially conjugated π system, said polymer being a dielectric.

9. The method of claim 7 further including exposing said solid solution to a solvent to dissolve those regions not exposed to said source of energy, said regions exposed to said source of energy substantially not being dissolved.

10. The method of claims 7 or 8, wherein said solvent is selected from the group consisting of N-methylpyrrolidinone (NMP), DMSO, DMF, CHCl_3 , CH_2Cl_2 and aqueous base.

11. The method of claim 7, wherein said solid solution is an electrical discharge layer for electron beam irradiation, the electron beam preferably being provided by a scanning electron microscope.

12. The method of claim 11, wherein said polymeric material has a surface conductivity greater than about 10^{-6} OHM^{-1} .

13. A structure comprising:

a substrate;

at least a part of a surface of said substrate having thereon a solid solution;

said solid solution containing materials selected from the group consisting of substituted and unsubstituted polyparaphenylenevinylenes, polyanilines, polyazines, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors, and combinations thereof and blends thereof with other polymers and containing a dissociated doping precursor selected from the group consisting of onium salts, iodonium salts, triflate salts, borate salts and tosylate salts and sulfonyloxyimides.

14. The structure of claim 13, wherein said substrate is a dielectric body housing an electronic device.

15. The structure of claims 13 or 14, further including a first resist material disposed between said surface and said solid solution.

16. The structure of anyone of claims 13 to 15, further including a resist material disposed over said solid solution.

17. A method comprising:

providing a surface at least a part of which is a dielectric;

disposing over at least a part of said surface a nonmetallic electrically conductive material containing a dissociated doping precursor, said nonmetallic electrically conductive material preferably being a polymeric material selected from the group consisting of substituted and unsubstituted polyparaphenylenevinylenes, polythiophenes, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors, combinations thereof and blends thereof with other polymers and containing a dissociated doping precursor being selected from the group consisting of onium salts, iodonium salts, triflate salts, borate salts, tosylate salts and sulfonyloxyimides, and exposing said surface with said nonmetallic conductive material thereon to an electron beam, said nonmetallic material substantially preventing charge accumulation on said surface.

18. The method of claim 17, wherein the conductivity of said material is greater than about 10^{-6} OHM^{-1} .

19. A resist comprising:

a polymeric composition selected from the group consisting of substituted and unsubstituted poly-paraphenylenevinylenes, polyarines, polythiophenes, polyazines, poly-p-phenylene sulfides, polyfuranes, polypyrroles, polyselenophenes, polyacetylenes formed from soluble precursors, combinations thereof and blends thereof with other polymers,

5 the solubility and electrical conductivity of said composition being dependent upon the presence of a dopant; and

a dopant precursor which generates said dopant upon exposure to energy, said precursor being selected from the group consisting of onium salts, iodonium salts, triflate salts, borate salts, tosylate salts and sulfonyloxyimides.

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FIG. 1

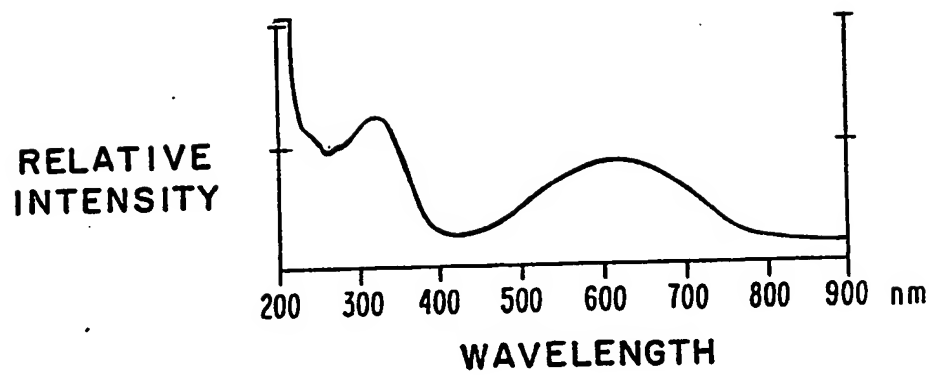


FIG. 2

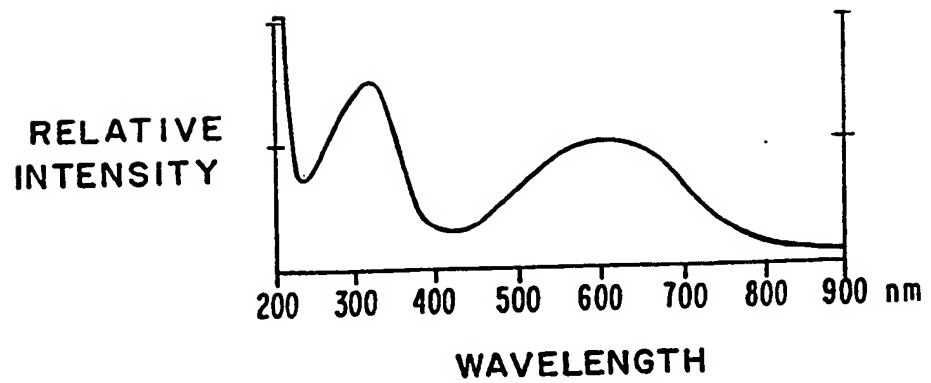


FIG. 3

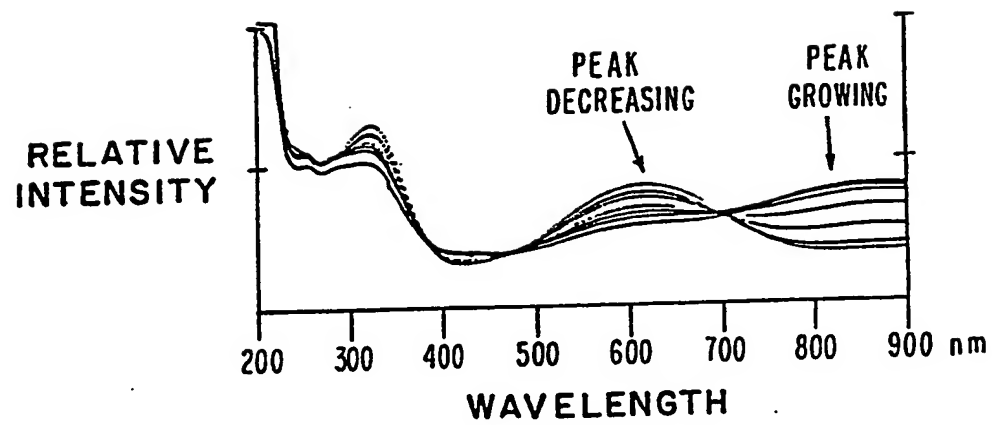


FIG. 4

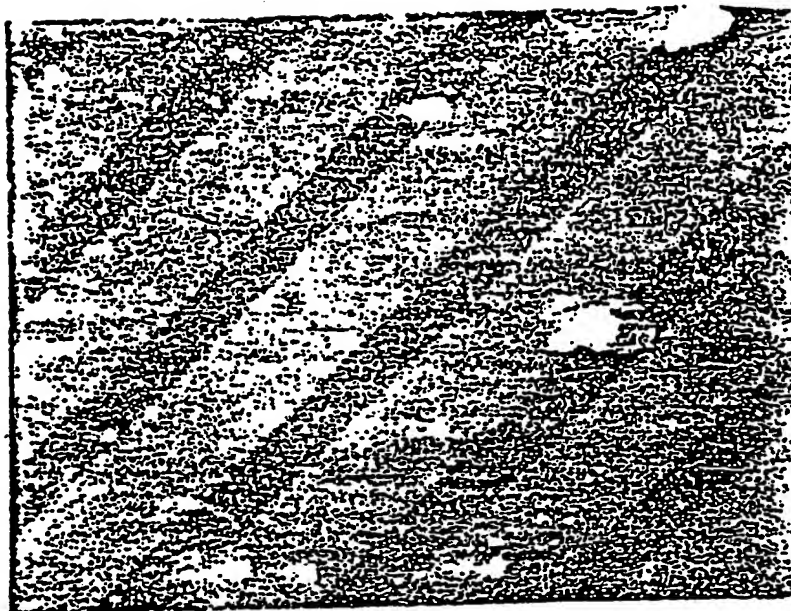


FIG. 5



FIG. 6

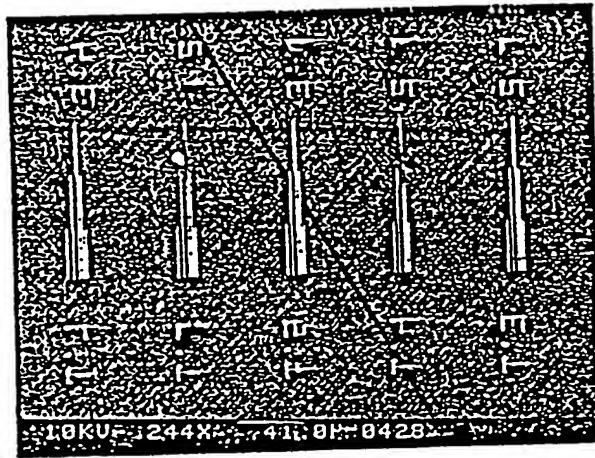


FIG. 7

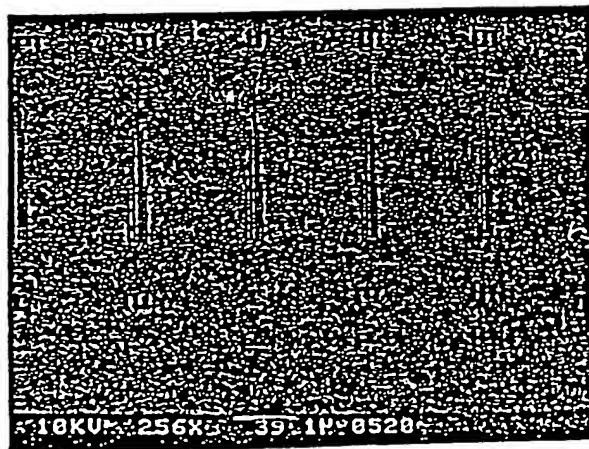


FIG. 8



FIG. 9

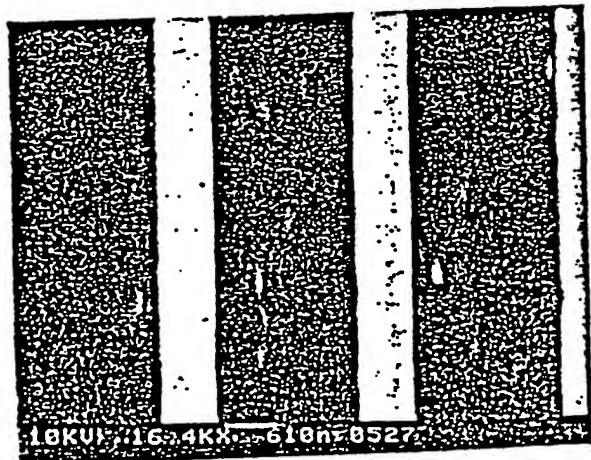
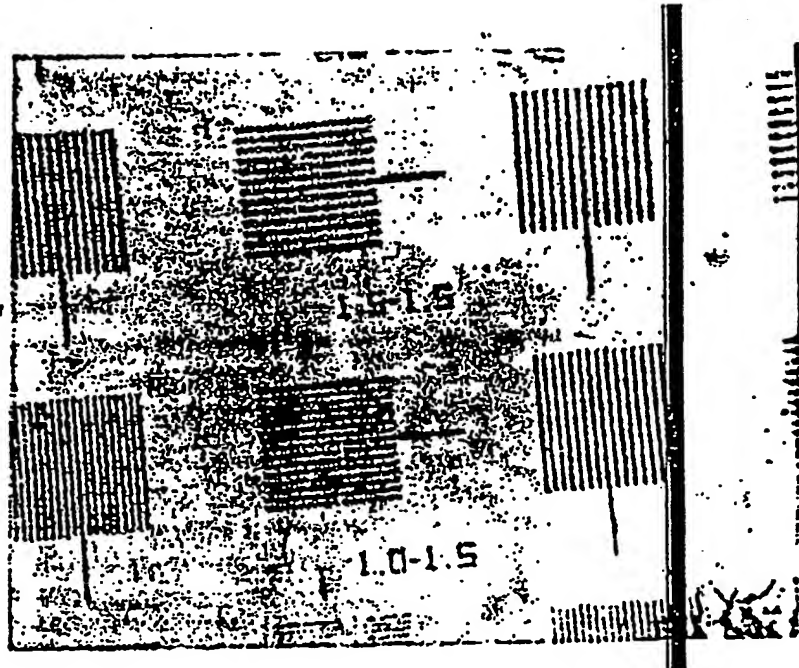


FIG. 10



Docket # MUH-12807

Applic. # _____

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